Kellogg/RL-53-259

THE M.W. KELLOGG COMPANY

Petroleum and Chemical Research Department

PROGRESS REPORT

ARCTIC RUBBER

U.S. Army Contract DA-44-109-qm-222
Project No. 7-93-15-604
For the Period October-December, 1952

January 1, 1953

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Petroleum and Chemical Research Department
Laboratory Division, Jersey City, N.J.

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Period Covered: October 1, 1952 to December 31, 1952

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Previous Reports on this Subject:

RL-50-139	dated	November 1, 1950
RL-51-146	"	February 1, 1951
RL-51-156	"	April 1, 1951
RL-51-163	"	July 1, 1951
RL-51-174	"	October 1, 1951
RL-52-183	"	February 1, 1952
RL-52-195	"	May 1, 1952
RL-52-209	"	August 1, 1952
RL-52-248	"	October 1, 1952

Approved:

E. F. Schwarzenbek

E. F. SCHWARZENBEK

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I. Introduction

A. Purpose of the Project

The primary purpose of this project is the development of a fluorine containing oil- and fuel-resistant elastomer which will retain its rubbery properties between -70°F. and +160°F. A more recent objective is the pilot plant production and large scale evaluation of the more promising elastomers, with special emphasis on the polymer currently designated by M. W. Kellogg as "X-300 Rubber".

B. Research Program

To achieve this goal, the M. W. Kellogg Co. has been authorized by the Quartermaster Corps to conduct a broad investigation of fluorocarbon polymers involving (1) monomer synthesis, (2) polymer preparation, and (3) polymer evaluation. Emphasis has been placed upon polymer preparation and especially upon the copolymerization of fluoroolefins and fluoro-chloro-olefins among themselves and with olefinic and diolefinic hydrocarbons.

Monomer synthesis at Kellogg has been restricted to products arising from the thermal dimerization of $CF_2=CFCl$, namely, $CF_2=CF-CF=CF_2$, $CF_2-CF=CF-CF_2$, and $CF_3-CF=CF_2$. Where feasible, the preparation of other monomers, e.g., $CF_2=CF_2$ and $CF_2=CHF$, has also been undertaken in these laboratories. For the most part, however, monomers not available commercially have been requested from Dr. Paul Tarrant of the University of Florida, Dr. Aldrich Syverson of the Ohio State University, and Dr. W. T. Miller of Cornell University, or obtained on an exchange basis from Minnesota Mining and Manufacturing Company.

Polymer preparation has proceeded through four phases: (a) exploratory copolymerization of new monomer pairs, (b) determination of the relative reactivities of monomers successfully copolymerized into elastomers, (c) synthesis of pound batches of these elastomers in several comonomer ratios for evaluation, and (d) pilot plant production of one elastomer (Kellogg "X-300 Rubber") which is of interest to the Quartermaster not so much as an Arctic Rubber but as an acid- and oxidant-resistant elastomer for protective suits, gloves, and boots.

Polymer compounding, testing, and evaluation has been carried forward most capably by Mr. C. B. Griffis and his staff at the Philadelphia Quartermaster Depot. The development of uses for X-300 has been the joint responsibility of Mr. Griffis and the Kellogg Applications Laboratory.

C. Past Progress

1. Quarters completed as of September 30, 1952: 9
2. Monomers available for copolymerization: 33

a.	Purchased	14
b.	Minnesota Mining & Mfg. Co.	3
c.	Dr. Tarrant	7
d.	Dr. Syverson	3
e.	M. W. Kellogg Co.	6

3. Copolymer systems investigated: 125
(where the numbers refer to the monomers listed in section III-A below):

1-3, 1-4, 1-5, 1-6, 1-7, 1-8, 1-9, 1-12, 1-13, 1-14, 1-16, 1-17, 1-18, 1-19, 1-20, 1-22, 1-23, 1-25, 1-27, 1-28, 1-30, 2-3, 2-4, 2-6, 2-8, 2-9, 2-12, 2-13, 2-15, 2-16, 2-17, 2-18, 2-19, 2-21, 2-22, 2-23, 2-24, 2-28, 2-29, 2-30, 2-32, 2-34, 3-4, 3-7, 3-9, 3-14, 3-18, 3-19, 3-20, 3-21, 3-22, 3-23, 3-24, 3-25, 3-30, 3-32, 4, 4-5, 4-6, 4-8, 4-9, 4-10, 4-11, 4-12, 4-14, 4-15, 4-19, 4-20, 4-21, 4-22, 4-24, 4-25, 4-27, 4-28, 4-29, 4-32, 5-9, 6-8, 6-9, 6-30, 8-13, 8-24, 9, 9-12, 9-13, 9-14, 9-16, 9-17, 9-18, 9-22, 9-23, 9-27, 9-28, 10-14, 10-28, 12-24, 13-17, 13-18, 14-22, 14-28, 16-18, 16-24, 17-18, 17-24, 19-22, 19-28, 20-22, 20-28, 21-28, 22, 22-24, 22-28, 23-28, 24-28, 24-31, 25-28, 27, 27-28, 28, 28-30, 28-32, and 30.

4. Rubberlike systems: 50

1-2, 1-3, 1-5, 1-13, 1-17, 1-22, 1-28, 2-4, 2-6, 2-13, 2-17, 2-22, 2-24, 2-28, 2-30, 2-32, 2-34, 3-4, 3-9, 3-14, 3-18, 3-19, 3-21, 3-22, 3-23, 3-24, 4-5, 4-28, 5-9, 9-12, 9-13, 9-17, 9-28, 12-28, 13-18, 14-22, 14-28, 17-18, 17-24, 20-22, 21-28, 22, 22-24, 22-28, 24-28, 24-31, 27-28, 28, 28-30, and 28-32.

5. Monomer reactivity ratios determined: 8

M_1	M_2	r_1	r_2
$CF_2=CF_2$	Butadiene	0.0	1.75
$CF_2=CFCl$	"	0.0	1.35
$CF_2=CCl_2$	"	0.0	0.80
$CF_2=CF-CF=CF_2$	"	0.0	1.35
$CF_2=CFCl$	Isoprene	0.1	1.41
$CF_2=CCl_2$	"	0.0	0.45
$CF_2=CF-CF=CF_2$	"	0.0	0.75
$CF_2=CFCl$	$CF_2=CH_2$	0.52	0.17

6. Status of rubberlike systems

   a. Most promising, ready for pilot plant and extensive tests: 1-2.

   b. Evaluated and rejected as unpromising: 1-3, 1-5, 3-9, 5-9, 22 and 28.

   c. Promising, should be evaluated: 1-13, 1-17, 1-22, 1-28, 2-22, 2-24, 2-30, 2-32, 2-34, 3-4, 3-24, 4-28, 9-13, 9-28, 12-28, 17-24, 22-24, 24-28, 24-31, and 28-32.

   d. Interesting but better recipes needed to increase yields or to increase proportion of fluorocarbon combined: 2-4, 2-28, 3-14, 3-18, 3-19, 3-21, 3-23, 14-22, 14-28, 21-28, 22-28, 27-28, and 28-30.

   e. Relatively uninteresting (low F content): 2-6, 2-13, 2-17, 3-22, 4-5 (isoprene copolymers no longer of interest), 9-12, 9-17, 13-18, 17-18, and 20-22.

7. Alfin and anionic (Na) polymerizations of fluoro-olefins unsuccessful.

8. No glass transition temperature noted for Teflon, "KEL-F", polyperfluorobutadiene, or polytrifluoroethylene from -150°C. to 85°C.

9. Vulcanization of "saturated" rubbers partially successful with Na_2S_x and peroxide-amine recipes.

10. Vulcanization of CF_2=CFCl/CH_2=CF_2 copolymer (X-300) successful with diisocyanates, apparently catalyzed by zinc oxide.

II. Summary of Current Progress

The number of monomers available for copolymerization studies has increased to 38, the number of copolymer systems investigated to 143, and the number of rubberlike systems to 61. Attempts to vulcanize the CF_2=CFH homopolymer and a 30/70 molar copolymer of CF_2=CFCl/n-butyl-acrylate have failed.

Considerable progress has been made in curing copolymers of CF_2=CFCl/CF_2=CH_2 (X-300 series) with diisocyanates. Physical properties of the vulcanizates have been determined and a comparison made of the 62/38, 50/50 and 30/70 molar CF_2=CFCl/CF_2=CH_2 copolymers. The 30/70 molar copolymer is at least as oil-resistant as the 50/50 and offers 6-9°C. advantage in TR-70 temperature. The 62/38 product, on the other hand, is not notably rubberlike.

Stepwise exposure of MDI vulcanizates of X-300 to higher temperatures has produced a material serviceable up to 537°F.

X-300 coated fabrics have been made successfully by cement coating, but calendering and extrusion await the development of softer, less "nervy" stocks.

Two vulcanizing agents have been synthesized for comparison with MDI. Metal oxides alone do not seem to cure X-300.

A small pilot plant has been erected for the experimental production of X-300 rubber. Operation is to begin in January, 1953. The entire output is committed to compounding and curing studies and to QM end item development.

III. Experimental Section

A. Monomer Synthesis

Thirty eight monomers are now available for copolymerization studies:

1. $CF_2=CFCl$
2. $CF_2=CH_2$
3. $CH_2=CH-CH=CH_2$
4. $CF_2=CF-CF=CF_2$
5. $CH_2=C(CH_3)-CH=CH_2$
6. $(CH_3)_2C=CH_2$
7. $CF_2-CF=CF-CF_2$
8. $CH_2=CHCl$
9. $CF_2=CCl_2$
10. $CH_3-CH=CH_2$
11. $C_6H_5-CH=CH_2$
12. $CH_2=CCl_2$
13. $CH_2=CCl-CH=CH_2$
14. $CF_3-CF=CF_2$
15. $CF_2=CF-CN$
16. $CH_2=CH-CN$
17. $CH_2=CH-COO\cdot C_4H_9$ (n)
18. $CF_2=CHCl$
19. $CF_3-CCl=CCl-CF_3$
20. $CF_3-C\equiv C-CF_3$
21. $CF_2=CHF$
22. $CH_2=CFCl$
23. cis $CF_3-CH=CH-CF_3$
24. $CF_2=CF_2$
25. trans $CF_3-CH=CH-CF_3$
26. $CH_2=CH-C_6H_4-CH=CH_2$
27. $CH_2=C(CF_3)(CH_3)$
28. $CH_2=CF-CH=CH_2$
29. $CF_2=C(CF_3)(CF_3)$
30. $CF_2=CFBr$
31. $CH_2=CH_2$
32. $CF_2=CCl-CF_3$
33. $CH_3-C(CF_3)=CH-COOH$
34. $CH_2=CH-CO-NH_2$
35. $CF_3-CH=CH_2$
36. $CH_2=CHBr$
37. $CF_2=CH-CH=CH_2$
38. $CF_3-CCl=CCl_2$

Dr. Tarrant has prepared one of the five new monomers:

(#37) $CF_2=CH-CH=CH_2$

This was a small, preliminary sample which polymerized extensively on standing.

Dr. Syverson furnished another of the new monomers:

(#35) $CF_3-CH=CH_2$ 148 g, b.p. -24° to -20°C.

The remaining monomers were purchased: $CH_2=CH-CO-NH_2$ (#34) from American Cyanamid, (#36) $CH_2=CHBr$ from Matheson and (#38) $CF_3-CCl=CCl_2$ from Halogen Chemicals, Inc.

B. Monomer Analyses

Monomer purity has become so critical in some cases that all monomers on hand are being analyzed with the mass spectrometer. A punched card file of all old and new monomers has been drawn up to aid in the identification of the various batches.

1. $CF_2=CFCl$ Tank No. 36M (M. W. Kellogg Co.)

$CF_2=CHCl$	0.25 Mol %
$CF_2=CFH$	<.04
N_2	1.51
O_2	0.34

2. $CF_2=CH_2$ Tank No. 858M-2-1 (General Chemical Div.)

N_2/CO	<0.04 Mol %

Chlorinated or fluorinated compounds of molecular weight greater than 64 - absent.

3. $CH_2=CFCl$ Tank No. 858M-22-1 (Tarrant)

B.P. -25° to -33°C

Propylene	1.6 Mol %
$CH_2=CF_2$, $CFH=CH_2$) & $CH_2=CCl_2$)	all very low

4. $CF_2=CFBr$ Tank 858M-30-1 (Tarrant)

B.P. -3.0° to -1.0°C.

$CF_2=CFBr$	95 Mol %
$CF_2=CFCl$	1.3
CO_2	2.9
$CO-N_2$	1.1
$CF_3-\overset{O}{\overset{\|}{C}}-Br$ (unident., possibly this)	0.8

5. $CF_2=CHCl$ Tank 858M-18-1 (M. W. Kellogg Company)

$CF_2=CHCl$	99.6 Mol %
$CF_2=CCl_2$	0.3
$C_2H_2F_3Cl$	0.06
$CF_2=CFCl$	0.02

6. $CH_2=CF-CH=CH_2$ Tank 858M-28-1 (Tarrant)

B.P. 10.5-13.0°C.

C_4H_5F	70%
C_4FH_7	30%

7. $CF_2=CF_2$ Tank 858M-24-1 (M. W. Kellogg Co.)

This sample contains no chlorine; there appears to be a small amount of hydrogen containing material present, concentration quite small. About 2% of N_2 or CO present.

8. $CF_3-CCl=CF_2$ Tank 858-32-1 (M. W. Kellogg Co.)

B.P. 6.8°C.

C_3F_5Cl	81.5 Mol %
air	17.9
C_3F_4Cl	0.3
$C_3HF_3Cl_2$ (?)	0.1
$C_2H_2F_2Cl_2$(?)	0.2

9. $CH_3-C(CF_3)=CH-COOH$ Tank 858M-33-1 (Tarrant)

Material on arrival was partly liquid and partly solid. The liquid was carefully decanted; a mass spectrogram for both the solid and liquid fractions confirmed the expected structure.

10. $CF_2=CFCl$ Tank 37M, 2nd cut (M. W. Kellogg Co.)

$CH_2=CHCl$	<0.01 Mol %
$CF_2=CHF$	0.89
$CFCl_3$	none
Higher molecular wt. than 116	none

11. $CF_2=CHCH=CH_2$ Preliminary (Tarrant)

$C_4F_2H_4$	92 Mol %
$CFCl=CFCl$	6
$C_4F_3H_3$ approx.	2

Note: It is not certain that the $C_4F_2H_4$ is the isomer listed; the mass spectrum does not necessarily support such a structure. Acetylenic bonds will be sought by other means.

12. $CF_2=CHF$ Tank 858M-21-1 (M. W. Kellogg Co.)

$CF_2=CClH$	0.06 Mol %
$CF_2Cl-CFHCl$	0.04
air	0.35

13. $CF_3CF=CF_2$ Tank 858M-14-2 (Tarrant)

$CF_3CF=CF_2$	94.2 Mol %
CO_2	3.9
N_2	0.3
unidentified impurity	1.5

14. $(CF_3)C{=}CH_2$ Tank 858M-29-1 (Minn. Mining & Mfg. Co.)

CO_2	0.3 Mol %
Cl compounds	absent

Sample gives mass spectrum of type expected for C_4F_8. There is a discrepancy in the mass spectrum at 113 m/c which may be due to about 0.2% of an unidentified compound.

Note: C_3F_6 cannot readily be detected in C_4F_8 by mass spectral means.

15. $CF_3CH{=}CH_2$ Tank 858M-35-1 (Syverson)

C_3H_6	0.1 Mol % maximum
Cl compounds	0.1 Mol % maximum, probably nil

Mass spectral pattern suggests CF_3- and $-CH{=}CH_2$ groupings in structure. Air cannot be detected in this compound satisfactorily by mass spectrometric means when present in small amounts. Sample is almost entirely $C_3F_3H_3$.

16. $CF_3-\underset{\underset{CH_3}{|}}{C}{=}CH_2$ Tank 858M-27-1 (Tarrant)

Chlorine compounds	<0.2 Mol %
$CF_3CH{=}CH_2$	<0.1
very little air	

Sample is almost entirely $C_4H_5F_3$; no C_4H_8 detectable.

17. $CF_2{=}CCl_2$ Tank 858M-9-1 (General Chem. Co.)

$CF_2{=}CCl_2$	98.1 Mol %
$CF_2{=}CHCl$	0.3
HCl	0.5
N_2	0.5
Unidentified impurity	<0.7

HCl content a maximum figure

18. $CH_2=CHBr$ Tank 858M-36-1 (Matheson)

$CH_2=CHBr$	83.6 Mol %
C_2H_5Br	13.7
$(C_2H_5)_2O$	1.5
CH_3-O-CH_3 (?)	0.4
C_2H_5Cl	0.1
C_2H_3Cl	0.1
$C_2H_2Cl_2$ (?)	0.2
HCl	0.4
$POCl_3$ (?)	0.1

C. Polymer Preparation

Copolymerizations have now been attempted with 143 systems (where the numbers refer to the monomers listed in Section III-A above):

1-2, 1-2-4, 1-2-9, 1-2-14, 1-2-21, 1-2-22, 1-2-24, 1-2-29, 1-2-30, 1-2-32, 1-3, 1-4, 1-5, 1-6, 1-7, 1-8, 1-9, 1-12, 1-13, 1-14, 1-16, 1-17, 1-18, 1-19, 1-20, 1-21, 1-22, 1-23, 1-25, 1-27, 1-28, 1-30, 2-3, 2-4, 2-6, 2-8, 2-9, 2-12, 2-13, 2-15, 2-16, 2-17, 2-18, 2-19, 2-21, 2-22, 2-23, 2-24, 2-28, 2-29, 2-30, 2-32, 2-34, 2-38, 3-4, 3-7, 3-9, 3-14, 3-18, 3-19, 3-20, 3-21, 3-22, 3-23, 3-24, 3-25, 3-30, 3-32, 4, 4-5, 4-6, 4-8, 4-9, 4-10, 4-11, 4-12, 4-14, 4-15, 4-17, 4-19, 4-20, 4-21, 4-22, 4-24, 4-25, 4-27, 4-28, 4-29, 4-32, 5-9, 6-8, 6-9, 6-30, 8-13. 8-24, 9, 9-12, 9-13, 9-14, 9-16, 9-17, 9-18, 9-22, 9-23, 9-27, 9-28, 10-14, 10-28, 12-24, 13-17, 13-18, 14-22, 14-28, 16-18, 16-24, 17-18, 17-24, 18-21, 19-22, 19-28, 20-22, 20-28, 21, 21-22, 21-28, 21-30, 22, 22-24, 22-28, 22-32, 22-38, 23-28, 24-28, 24-31, 25-28, 27, 27-28, 28, 28-30, 28-32, 30, and 37.

Sixty-one of these systems can be considered rubberlike: 1-2, 1-2-14, 1-2-21, 1-2-22, 1-2-24, 1-2-29, 1-2-30, 1-2-32, 1-3, 1-5, 1-13, 1-17, 1-22, 1-28, 2-4, 2-6, 2-13, 2-17, 2-22, 2-24, 2-28, 2-30, 2-32, 2-34, 3-4, 3-9, 3-14, 3-18, 3-19, 3-21, 3-22, 3-23, 3-24, 4-5, 4-28, 5-9, 9-12, 9-13, 9-17, 9-28, 12-28, 13-18, 14-22, 14-28, 17-18, 17-24, 20-22, 21, 21-22, 21-28, 22, 22-24, 22-28, 22-32, 24-28, 24-31, 27-28, 28, 28-30, 28-32, and 37.

Recent experimental data relative to many of these systems are set forth below (see Sections III-D-3, III-E for a detailed report on the 1-2 system).

1. $CF_2=CH-CH=CH_2$ (#37) Copolymers

When received from Dr. Tarrant, the first sample of this monomer had polymerized extensively. The product was not particularly rubbery (Table 1) but a more complete evaluation of this homopolymer and its copolymers will be made when a larger sample of monomer becomes available.

2. $CF_2=CFCl/CF_2=CH_2/X$ Terpolymers

An attempt has been made to improve the low temperature properties by incorporating into the chain small amounts (up to 20 mole %) of a third monomer. The 1-2-21, 1-2-22, 1-2-24, 1-2-29, 1-2-30, and 1-2-32 combinations have produced rubbery products. These are listed in Table 2. Present plans call for preparation of larger samples of these terpolymers for evaluation.

3. Miscellaneous Exploratory Copolymerizations

Results of recent exploratory studies are shown in Table 1. None of these products, with the possible exception of 22-32, can be considered interesting enough to warrant further evaluation (i.e., rubbery materials obtained in good yield with a reasonable amount of each monomer combined).

D. Polymer Evaluation (by and with Mr. C. B. Griffis of the Philadelphia Quartermaster Depot)

1. Vulcanization of $CF_2=CFH$ (#21) Homopolymer

A sample of this polymer was sent to the Depot for vulcanization with MDI. Mixing proved difficult because of the stiffness of the polymer. Little or no reaction with MDI occurred. (The "cured" polymer was just as soluble in acetone as the uncured.)

2. Acrylate (#17) Copolymers

A 30/70 molar $CF_2=CFCl$/n-butyl acrylate (1-17) copolymer sent to the Depot failed to react with a variety of curatives. Because of its poor oil-resistance, this series will probably not be considered further.

TABLE 1

MISCELLANEOUS EXPLORATORY COPOLYMERIZATIONS

Run No.	System	Comonomers	Moles Charged	Moles Combined	Recipe	% Conversion	Hrs. Polymerization	Appearance
763	1-17	CF_2=CFCl/CH_2=CH-CO_2-CH_3	50/50	35/65	/a/	72	5	slightly rubbery
844	1-21	CF_2=CFCl/CF_2=CFH	50/50	—	/a/	98	24	powder
772	21-18	CF_2=CFH/CF_2=CHCl	50/50	69/31	/a/	14	69	gum
774	3-18	CH_2=CH-CH=CH_2/CF_2=CHCl	50/50	—	/b/	0	1176	—
775	3-19	CH_2=CH-CH=CH_2/CF_3-CCl=CCl-CF_3	50/50	—	/b/	0	1176	—
776	3-21	CH_2=CH-CH=CH_2/CF_2=CFH	48/52	—	/b/	0	1176	—
777	3-23	CH_2=CH-CH=CH_2/CF_3-CH=CH-CF_3 (cis)	50/50	—	/b/	0	1176	—
781	22-21	CH_2=CFCl/CF_2=CFH	50/50	81/19	/a/	16	24	tacky rubber
783	38-2	CF_3-CCl=CCl_2/CF_2=CH_2	50/50	—	/a/	1	24	powder
784	38-22	CF_3-CCl=CCl_2/CH_2=CFCl	50/50	—	/a/	8	24	putty-like
782	22-32	CH_2=CFCl/CF_3-CCl=CF_2	50/50	93/7	/a/	32	24	tacky rubber
842	21-30	CF_2=CFH/CF_2=CFBr	50/50	42/58	/a/	43	24	powder
843	1-30	CF_2=CFCl/CF_2=CFBr	50/50	50/50	/a/	85	24	powder
858	37 /c/	CF_2=CH-CH=CH_2	41.2% F. found; 42.2% theory.					slightly rubbery
845	21	CF_2=CFH	100/0	—	/a/	93	24	powder

/a/ Persulfate-bisulfite suspension at 20°C.
/b/ Mass polymerization at -15°C. with 1% $(CCl_3$-CO-O$)_2$
/c/ Spontaneous polymerization en route from Univ. of Florida

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TABLE 2

CF_2=CFCl/CF_2=CH_2/X TERPOLYMERS

MOLES CF_2=CFCl/CF_2=CH_2/X CHARGED: 40/40/20

Code	System	Termonomers (X)	Recipe	Moles CF_2=CFCl/ CF_2=CH_2/X Combined	% Conversion	Hrs. Polymerization	Appearance
766	1-2-21	CF_2=CFH	/a/	—	100	24	rubbery
854	1-2-22	CH_2=CFCl	/a/	38/31/25 /b/	62	2	snappy rubber
880	1-2-24	CF_2=CF_2	/a/	42/41/17	23	5	slightly rubbery
951	1-2-29	CF_2=C(CF_3)$_2$	/a/	52/45/3	63	24	snappy rubber
767	1-2-30	CF_2=CFBr	/a/	39/42/19	100	24	tough rubber
770	1-2-32	CF_3-CCl=CF_2	/a/	37/42/21	78	69	rubber

/a/ Persulfate - bisulfite suspension at 20°C.
/b/ One possible interpretation of F and Cl analyses.

FILE NO.: LAS-42
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3. CF_2=$CFCl$/CF_2=CH_2(1-2) Copolymers (Kellogg X-300 Rubber)

a. Review of Properties

On November 4, Mr. C. B. Griffis submitted a comprehensive report in which he consolidated all the information available at the Philadelphia QM Depot Laboratories on CF_2=$CFCl$/CF_2=CH_2 copolymers. These data are summarized in Tables 3, 4, 5, 6, and 7.

Compounding recipes for X-300 rubber (nominally 50/50 molar CF_2=$CFCl$/CF_2=CH_2) are set forth in Table 3; compounding recipes for the alternate 62/38 and 30/70 molar ratios are summarized in Table 4.

The results of a cure study on five X-300 stocks are given in Table 5. Two of these stocks were vulcanized with MDI, methylene bis(p-phenyl isocyanate)(1F78 and 1F55, with and without ZnO, respectively); two others were vulcanized with TDI, toluene-2, 4-diisocyanate (1F44 and 1F54, with and without ZnO, respectively); the fifth was filled with Hi-Sil C and cured with MDI and ZnO (1F79). All stocks were press molded successfully at 212° and 260°F. At higher temperatures, viz., 287°, 300°, 320°, and 340°F., the stocks showed an increasing tendency to blister. Stocks made without ZnO molded well at 300°F. The role of ZnO in the diisocyanate cure is not yet clear; there is some indication that ZnO accelerates the cure (cf. Table 5) and that it improves processibility. Nonetheless, lead oxide and well known vinyl stabilizers are being studied as replacements.

The oven cure which follows press-molding must be done carefully to avoid blistering. Normally, this cure can be accomplished at 212°F. without difficulty.

Test results and aging data on an MDI-ZnO-cured X-300 stock (1F78) are set forth in Table 6. The resistance of X-300 to hydrocarbons, red fuming nitric acid, oxygen, and ozone is excellent. The low temperature stiffness and compression set properties, on the other hand, require considerable improvement.

Better low temperature properties, with very little sacrifice in oil resistance, can be attained by increasing the CF_2=CH_2 content from the normal 50 mole % to 70 mole %, (cf. Table 7). Plans have been made for a more intensive study of both the 30/70 and 20/80 molar CF_2=$CFCl$/CF_2=CH_2 copolymers. Varying the copolymer composition in the opposite direction, i.e., toward a higher CF_2=$CFCl$ content, leads to excessively stiff products. The aromatic (SR-6) resistance of the 62/38 molar CF_2=$CFCl$/CF_2=CH_2 vulcanizate (1F87) is surprising. This value has been confirmed with a new compound but not with a new batch of polymer.

TABLE 3

COMPOUNDING RECIPES USED FOR X-300*

GM Compound No.	1F15	1F16	1F17	1F24	1F28	1F29	1F44	1F45	1F46	1F47	1F48
X-300 Blend	100	100	100	100	100	100	100	100	100	100	100
Philblack "O"	40	40	40								
Red Lead	10		10								
GMF	2		2								
Triethylene Tetramine	2	2									
XLC Magnesia	15										
Zinc Oxide		5	10				5	5	5	5	5
Stearic Acid		3	3							5	
Sulfur		2									
Thionex		0.4									
DPG		0.2									2
Kel-Flo Blend				15	10						
Benzoyl Peroxide				15	3						
Hydrophobic Silica						15					
Toluene-2, 4-Diisocyanate							5				
4-4'-diamino diphenylmethane								5			
Methylene bis (4-phenylisocyanate)									5	5	5
Cure Temp., °F., for molding	300	300	300	300	300	300	212	212	212	320	320
	Hard tough sheet - not cured. No test.	Hard tough sheet - not cured. No test.	Hard tough sheet - not cured. No test.	Flexible sheet - no cure after 40' @ 300°F., plus 4 hours @ 350°F. No test.	Flexible sheet - no cure after 30' @ 300°F., plus 4 hours @ 350°F. No test.	Flexible sheet - no cure after 30' @ 300°F., plus 4 hours @ 350°F. No test.	Cured sheet - see test results.	Not cured.	Cured sheet.	Not cured - stocks bubbled in mold. No test.	Not cured - stocks bubbled in mold. No test.

*(X-300 made of blends of M.W. Kellogg "G" Polymer Numbers 328, 449, 450, 451, 453, 640, 654, 655, 636, 635, 668, 663, 667, 668)

GM Compound No.	1F54	1F55	1F69	1F70	1F71	1F68	1F72	1F73	1F74	1F86	1F87
X-300 Blend	100	100	100	100	100	100	100	100	100	100	100
Toluene-2, 4-diisocyanate	5										
Methylene bis (4-phenylisocyanate)		5	5	10	5	10	5	10	15	5	10
Zinc Oxide			5	5	5	5	5	5	10	5	5
Philblack "O"			20	20			10	10	10		
Hi-Sil "C"					20	20				30	30
Cure Temp., °F., for molding	300	300	340	340	340	340	220	220	220	287	287
	Cured. See table 5.	Cured. See table 5.	Cured - stock full of bubbles.	Cured - stock full of bubbles.	Cured - stock full of bubbles.	Cured - stock full of bubbles.	Cured - stock full of bubbles.	Cured - stock full of bubbles.	Cured - full of bubbles.	Cured. Stiff stocks.	Cured. Stiff stocks.

GM Compound No.	1F77	1F78	1F79	1F80	1F81	1F86	1F88	1F89	1F90	1F91	
X-300 Blend	100	100	100	100	100	100	100	100	100	100	
Methylene bis (4-phenylisocyanate	5	5	5	3	5	5		5	5	5	
Zinc Oxide	5	5	5	5	5	5	5				
Hi-Sil "C"	10		15		10	10					
Chrome Yellow					10						
Philblack "O"					2	3					
Flexol TOF						20					
Mapico Yellow Lemon						12					
Octadecylisocyanate							5				
Lead Oxide								5			
Tri-Mal									5		
Vanstay										5	
Cure Temp., °F., for molding	260	260	220	260	260	260	260	260	260	260	
	Stock full of bubbles. No good for test.	Cured - good stock. See table 5.	Cured - good stock. See table 5.	Cured - good stock.	Cured - good stock. Used for coating.	Stock not cured. Color not charred by HNO_3	Not cured - same isocyanate.	Heat resistant	compounding stuff	results not in.	

TABLE 4

COMPOUNDING RECIPES USED FOR 62/38 and 30/70 MOLAR
CF_2-$CFCl$/CF_2-CH_2 COPOLYMERS

QM Compound No.	1F18	1F19	1F20	1F22	1F26	1F87	1F82	1F83	1F85	1F84
62/38 Blend	100	100	100	100	100	100				
30/70 Blend							100	100	100	100
Philblack "O"	30	30	30	20						
Stearic Acid	1	1	1							
Sulfur	2									
ZL-109	10	5	3							
Na_2S_x		5		3						
Hydrogenated liquid polybutadiene				15						
Triethylene tetramine					3					
KEL-FLO Blend					5					
Benzoyl Peroxide					5					
Methylene bis (4-phenylisocyanate)						5	5	8	5	5
Zinc Oxide						5	5	5	5	5
KEL-F Plasticizer 149-28							5	5		
Flexol TOF									15	
Hi-Sil "C"									10	
Cure Temp., °F., for molding	340	340	340	300	300	260	260	260	260	260
	ZL-109 not compatible. No stock.	ZL-109 not compatible. No stock.	Hard, brittle sheet. Could not test.	Hydrogeneted liquid polybutadiene not compatible.	Reacted violently on mill. No cure - stock spongy.	Good stock. See Table 7.	Poor stock.	Poor stock.	Poor stock - could not test.	Stock stuck to mold - mold release used. See Table 7.

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THE M. W. KELLOGG COMPANY
Petroleum & Chemical
Research Dept.
Jersey City, N. J.

TABLE 5

TEST RESULTS - X-300 CURE STUDY

QM Compound No.	1F78	1F44	1F79	1F54	1F55
Temp., °F., for molding	220	212	220	300	300
Time in mold (min.)	60	20	120	120	120
Condition of samples from press	Good	Good	Good		
Tensile Strength, psi					
Press cure	700	900	1600	380	325
+3 hrs at 160°F.	450		1600		
+16 hrs at 160°F.	700		1950		
+3 hrs at 160°F. +3 hrs. at 212°F.	700				
+3 hrs at 160°F. + 16 hrs. at 212°F.	1800				
+3 hrs at 212°F.	725	1050	Bubbles	400	400
+16 hrs at 212°F.	1550	1700	Bubbles	700	700
Elongation, percent					
Press cure	1200	600	350	1000	1000
+3 hrs at 160°F.	440		320		
+16 hrs at 160°F.	380		350		
+3 hrs at 160°F. + 3 hrs at 212°F.	380				
+3 hrs at 160°F. + 16 hrs at 212°F.	360				
+3 hrs at 212°F.	390	600	Bubbles	1100	1050
+16 hrs at 212°F.	350	580	Bubbles	950	800
Stress at 300% Elongation					
Press cure	150	300	1500	150	150
+3 hrs at 160°F.	300		1550		
+16 hrs at 160°F.	450		1750		
+3 hrs at 160°F. + 3 hrs at 212°F.	500				
+3 hrs at 160°F. + 16 hrs at 212°F.	1000				
+3 hrs at 212°F.	400	350	Bubbles	150	150
+16 hrs at 212°F.	950	350	Bubbles	150	175
Hardness, Shore "A", 5 sec.					
Press cure	55	58	68	62	59
+3 hrs at 160°F.	55		71		
+16 hrs at 160°F.	59		71		
+3 hrs at 160°F. + 3 hrs at 212°F.	60				
+3 hrs at 160°F. + 16 hrs at 212°F.	61				
+3 hrs at 212°F.	59	58	Bubbles	62	58
+16 hrs at 212°F.	59	58	Bubbles	59	58

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TABLE 6

TEST RESULTS ON STOCK 1F78 (X-300)

	2 Hours in RFNA /1/		7 days in Ox Bomb /2/		Ozone Exposure /3/	
	Before	After	Before	After	Before	After
Tensile Strength, psi	1800	1700	1500	1600	1500	1550
Elongation, percent	360	410	350	345	320	330
Stress at 300%, psi	1000	700	900	900	1100	1100
Hardness, Shore "A", 5 sec.	61	60	61	62	59	60

Volume Swell	
in SR-6	0.84
in SR-10	0.05
Compression Set	
73 ± 3°F.	
10" recovery (set)	48
30' recovery (set)	35
158°F.	
10" recovery (set)	98
30' recovery (set)	98
Brittle Point, °C.	-51
Retraction Test	
Initial Elongation, %	200
TR-10 (minus °C.)	15.8
TR-30 "	13.4
TR-50 "	12.1
TR-70 "	+3
Gehman Stiffness	
T-100 (minus °C.)	10
T-10 "	3
T-5 "	1
T-2 "	+2

/1/ RFNA = Red fuming nitric acid - full immersion.
/2/ ZZ-R-601 procedures.
/3/ Conducted at Bureau of Standards - 6 hours in 130 ppm ozone.

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TABLE 7

TEST RESULTS ON ALTERNATE CF_2=$CFCl$/CF_2=CH_2 RATIO COPOLYMERS

QM Compound No.	1F87	1F78	1F84
Copolymer Ratio CF_2=$CFCl$/CF_2=CH_2	62/38 /a/	50/50 /b/	30/70 /c/
Press cure, time (min)/Temp. (°F.)	60/260	60/260	60/260
Air oven cure after press cure	3 hrs at 160 +16 hrs at 212	3 hrs at 160 +16 hrs at 212	3 hrs at 160 +16 hrs at 212
Tensile Strength, psi	1730	1800	1350
Elongation, %	200	360	620
Stress at 300% Elongation, psi	-	1000	700
Hardness, Shore "A", 5 sec.	81	61	62
Retraction Test			
Initial Elongation, %	100	200	200
TR-10 (minus °C.)	+17.5	15.8	27
TR-30 "	+21.	13.4	23
TR-50 "	+23.3	12.1	11
TR-70 "	+25.3	+3	6.5
Gehman Test			
T100 (minus °C.)	32	10.5	30
T10 "	+13	3.5	18
T5 "	+17	1	13
T2 "	+21	+1.5	5
Volume Swell, %			
in SR-6	18.1	0.84	3.2
in SR-10	2.2	0.05	0.7

/a/ 62/38 copolymer blends of 712-G and 718-G
/b/ 50/50 X-300
/c/ 30/70 copolymer blends of 681-682-684

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Additional X-300 developments reported by QM:

(1) Toxicity: X-300 has been cleared officially by the Surgeon General (Army) for use in outer garments.

(2) Cohesive Energy Density: According to swelling measurements in a series of organic liquids, the $(C.E.D.)^{1/2}$ of X-300 is 9.3-9.9, an ideal value for an oil resistant rubber.

(3) Resistance to Fungi: No evidence of growth on X-300.

(4) Plasticizers: Flexol TOF (trioctylphosphates), an excellent low temperature plasticizer, is compatible with X-300, but interferes with MDI vulcanization.

(5) Pigments: The OD color obtained with iron yellow pigment is unaffected by RFNA.

(6) Coated Fabric: Glass cloth has been successfully spread coated with X-300 cement.

b. Heat Resistant Stocks

$CF_2=CFCl/CF_2=CH_2$ copolymers are in themselves quite heat resistant, but difficulties have been encountered in attempting to age MDI vulcanizates above 300°F. Three stocks referred to in Table 3 as 1F89, 1F90, and 1F91 have been oven cured for three hours at 160°F. + 16 hours at 212°F. and oven aged at 400° and 480°F. In every case, the MDI seemed to break down and act as a blowing agent. On the other hand, a step-wise exposure of the stocks to higher temperatures (up to 537°F.) could be accomplished without any sign of blistering and with good retention of tensile strength. Apparently the MDI vulcanization is incomplete even after 16 hours at 212°F.

c. Fabric Coating at Hodgman Rubber Company

In October eleven pounds of X-300 were shipped to Mr. Griffis for compounding, coating, and calendering experiments at the Hodgman Rubber Company, Framingham, Massachusetts, in cooperation with Mr. Joseph L. Haas, Technical Director.

Four X-300 stocks were made up to be calendered onto cotton, nylon, orlon, and glass cloth:

	A	B	C	D
X-300, pts. by wt.	100	100	100	100
MDI	5	5	5	5
ZnO	5	5	5	5
1001 (phenolic) resin	10			
Butyl Rubber No. 15			5	10

Stock A calendered satisfactorily with the top roll at 250°F., the face roll at 250°F., and the bottom roll at 240°F. (With five parts Butyl-15, stock A calendered exceptionally well.) Stocks B, C, and D calendered poorly.

Stock A could be picked up with cotton, but not with orlon, nylon, or glass. After being anchor coated on both sides with a cement made from stock B, orlon, nylon, and glass could be calendered with stock A containing five parts Butyl-15, but on the whole no acceptable calendered fabrics were obtained. An exceptionally good four mil free film was obtained; however it is being tested for nitric acid permeability at Connecticut Hard Rubber Company.

At Mr. Haas' request, three pounds of X-300 were left at Hodgman Rubber for evaluation in a series of oxide compounds:

	E	F	G	H
X-300, pts. by wt.	100	100	100	100
Litharge	30	-	-	-
MgO	-	30	-	-
Trimal	-	-	30	-
ZnO	-	-	-	5
Stearic Acid	2.5	2.5	2.5	2.5

Four additional stocks were made up by adding five parts MDI to the above. These stocks were designated EE, FF, GG and HH, respectively. All stocks were press-cured one hour at 260°F. and tested before and after an additional oven cure of 16 hours at 260°F. (The suffix "1" in the following table denotes the oven-cured sample.)

	Tensile	Elongation
E	760 psi	200%
E-1	670	400
EE	775	250
EE-1	935	475
F	1750	300
F-1	1600	300
FF	2275	175
FF-1	1600	225
G	1250	350
G-1	670	350
GG	1800	300
GG-1	1275	400
H	1190	375
H-1	1060	375
HH	735	400

The magnesia-filled stocks were notably stronger than the others, but all of the oxide compounds (E, F, G, H) dispersed in acetone. Apparently the oxides acted as reinforcing agents rather than cross-linking agents.

d. Improved Vulcanizing Agents for X-300 Rubber

Although MDI seems to cross-link X-300, its rate of reaction and compatibility with the polymer are not wholly satisfactory. Synthesis of other difunctional reagents potentially capable of reacting with the polymer has been initiated. Two of these compounds (105-35 and 180-56) have been sent to the Depot for comparison with MDI.

All of Mr. Griffis' cures have been carried out with du Pont MDI, a dark liquid, approximately 90% pure. Recently, he has tested Monsanto MDI-100, a reasonably pure, crystalline compound. Although MDI-100 was easier to add to X-300 on the mill, no great improvement was noted in the rate of cure.

Although X-300 MDI stocks require an oven cure for the full development of physical properties, the weight loss in this operation is negligible. Compounds 1F78, 1F87, and 1F93 (cf. Table 3) lost 0.1-0.2% in weight after three hours at 160°F., and 0.2-0.3% after 16 hours at 212°F.

E. Pilot Plant Operations - X-300 Rubber

A small pilot plant has been erected and four batches of X-300 made toward the end of this quarter. Analyses are not yet available. A number of preliminary runs will have to be made in this equipment before difficulties encountered in monomer charging, recipe, balance, overall reaction rate and product quality control are fully resolved. All reasonably homogeneous batches having a combined $CF_2{=}CFCl/CF_2{=}CH_2$ molar ratio between 45/55 and 53/47 will be considered satisfactory for shipment to QM.

1. X-300 Quality Control

Samples of gum and ZnO-MDI-compounded X-300 are to be checked in a Mooney viscometer at Scott Testers, Inc. If these tests are successful, an instrument will be purchased for product quality control and compounding studies.

IV. Plans for Future Work

1. Pilot plant production of X-300 for thorough evaluation in a variety of end items (of immediate interest: protective suits, hoods, gloves, and boots).

2. Development of improved X-300 compounds for calendering and extrusion.

3. Evaluation of pound batches of the more promising rubbers noted in the "Past Progress" section

4. Exploratory polymerization of new monomer pairs and development of better recipes where needed to improve yields.

F. J. HONN

J. M. HOYT

References to Original Records:

Notebook #135 (A. N. Bolstad) pp. 151-174
Notebook #168 (J. M. Hoyt) pp. 111-142
Notebook #173 (R. E. Martin) pp. 193-199
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Notebook #202 (F. N. Roberts) pp. 1-47
Notebook #196 (W. M. Sims) pp. 52-61